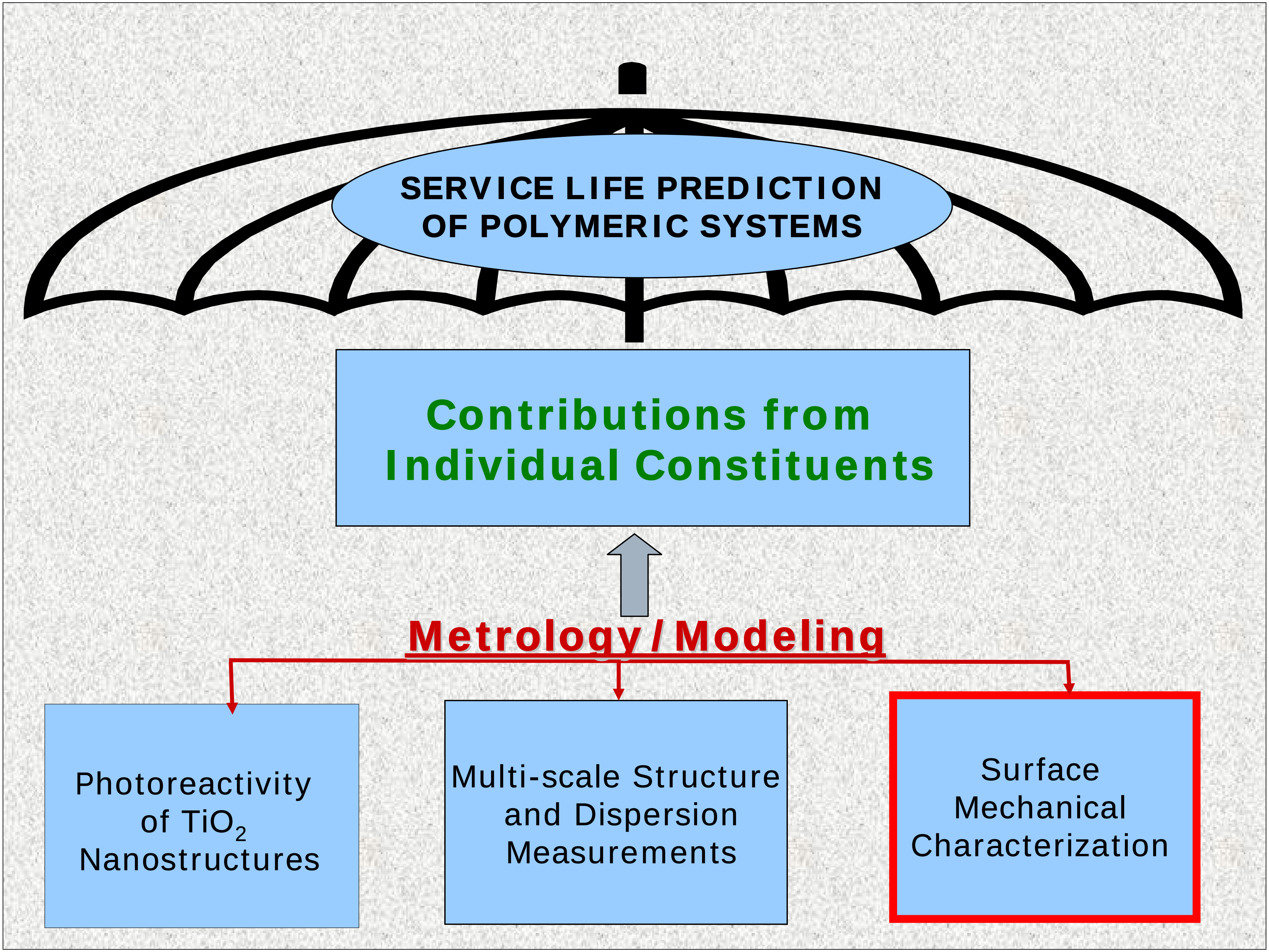
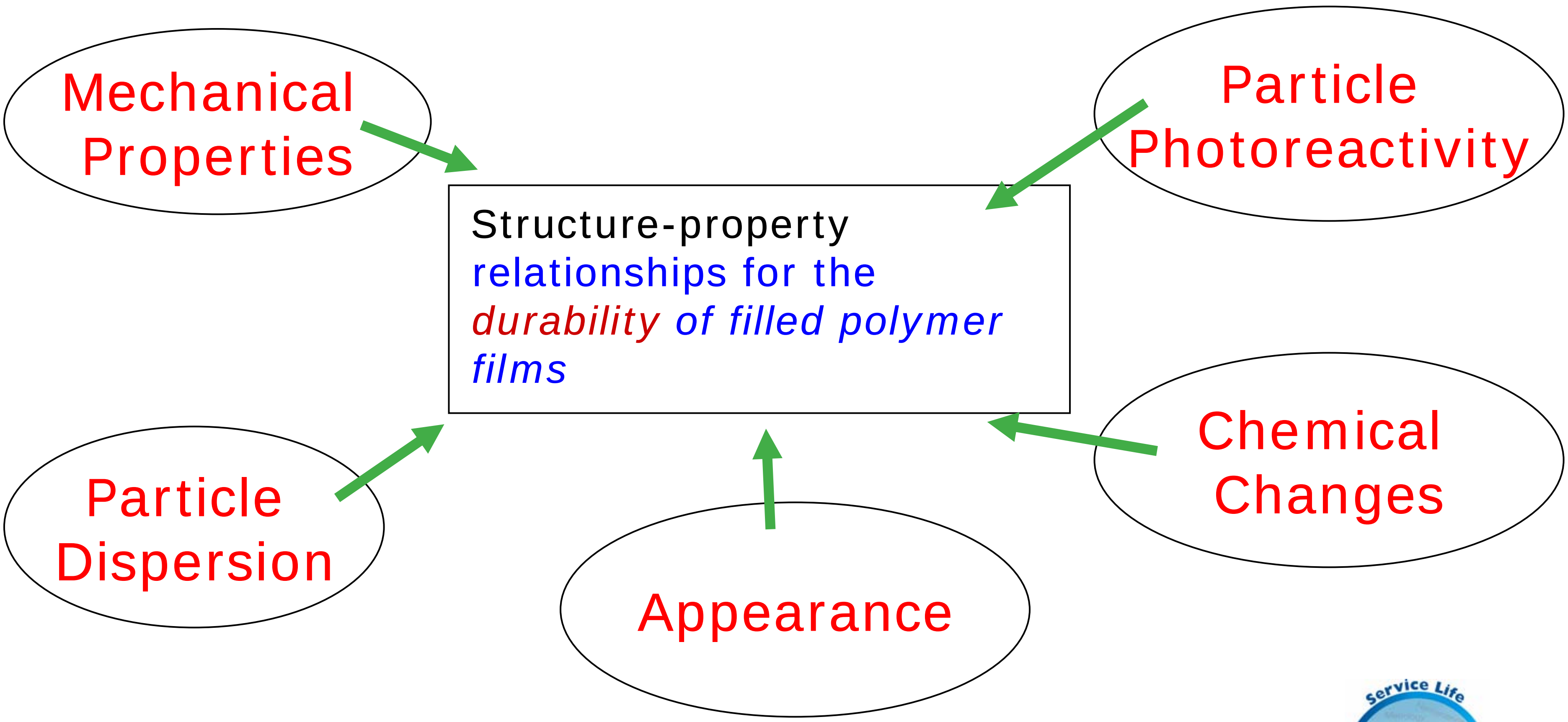

SERVICE LIFE PREDICTION
OF POLYMERIC SYSTEMS
Contributions from
Individual Constituents
Metrology / Modeling
Photoreactivity
of TiO_2
Nanostructures
Multi-scale Structure
and Dispersion
Measurements
Surface
Mechanical
Characterization

Mechanical Property Characterization of Polymer Film Surfaces and Interfaces

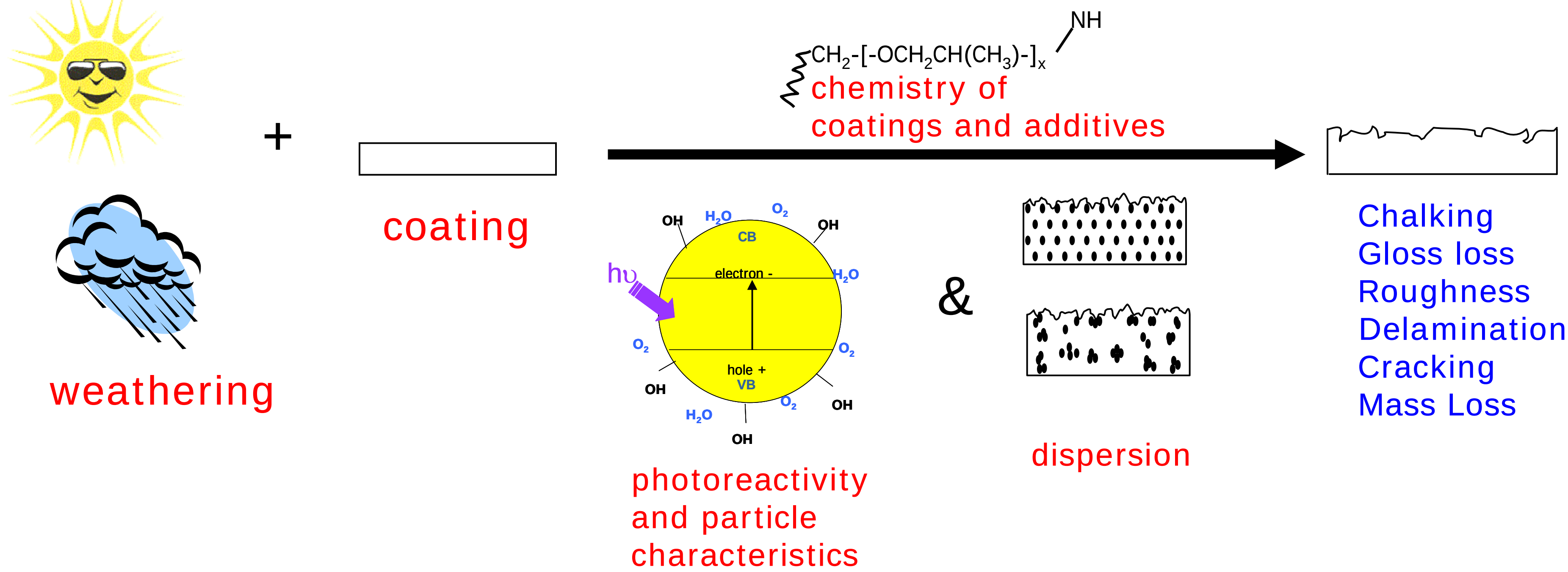
Aaron M. Forster

Constituent Contribution to Service Life Prediction

New Technical Idea



What is the Problem?



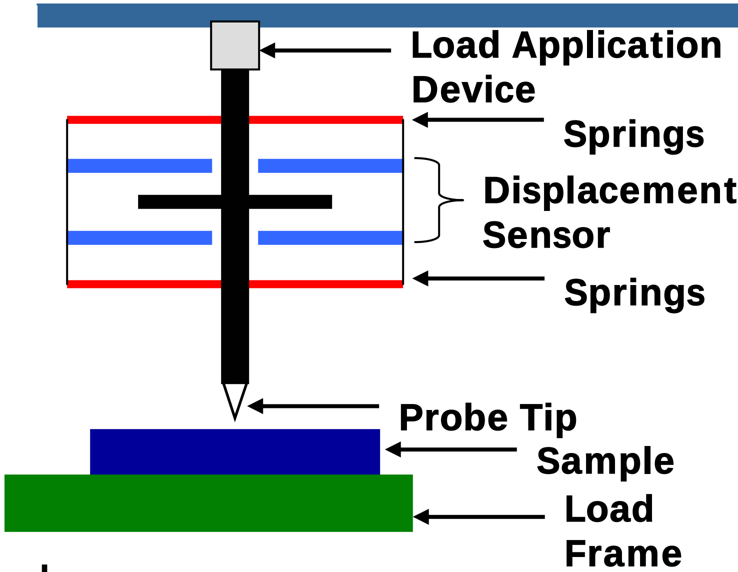
- Dispersion, Photoreactivity, Matrix Chemistry (micro and nano-scale) contribute to the chemical, mechanical, and physical changes that are associated with macroscale coating degradation

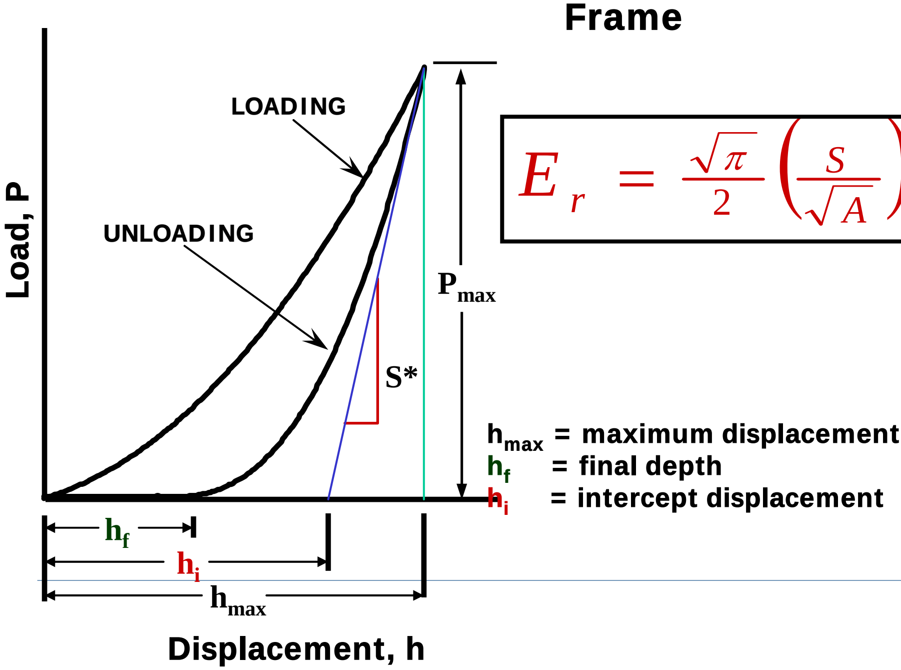
Why Nanoindentation?

- Difficult to accurately measure the mechanical properties of small volumes at the surface of polymer films
  - **Nanoindentation**
  - Brillouin Light Scattering
  - Quartz Crystal Microbalance
  - Other Acoustic Methods

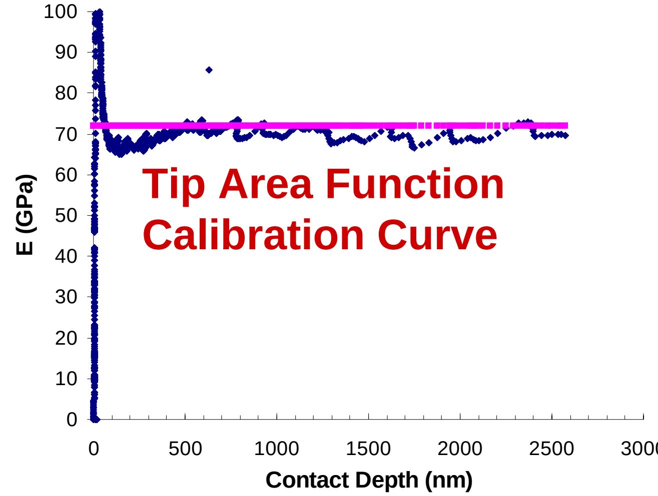
- Nanoindentation or Instrumented indentation testing (IIT) can provide mechanical property data at length scales that are several orders of magnitude less than bulk. micron size spatial resolution across exposed surface
  - measure 1 μm to 3 μm into surface
  - quantify a range of elastic and viscoelastic properties

Principles of Indentation





$$E_r = \frac{\sqrt{\pi}}{2}\left(\frac{S}{\sqrt{A}}\right)$$

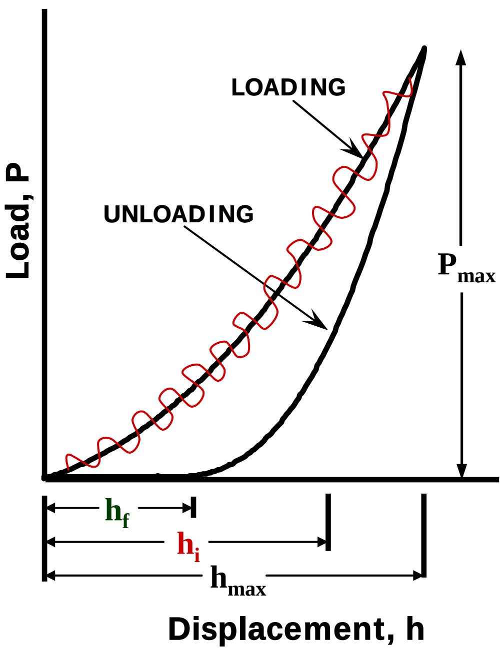


MTS Nano XP/CSM

- **Travel = 2 mm**
- **Displ. Res. = < 0.01 nm**
- **Max Load = 1 kg**
- **Load Res. = 50 nN**

Quasi-static / Dynamic

Continuous Stiffness Method



h_{max} = maximum displacement
h_f = final depth
h_i = intercept displacement

$$E_r = \frac{\sqrt{\pi}}{2}\left(\frac{S}{\sqrt{A}}\right)$$

- Dynamic oscillation is superposed over a given loading history
- Settings:
  - harmonic amplitude = 1-50 nm
    frequency target = 10-250 Hz
- Better sensitivity to surface contact, provides continuous estimate of E

Dynamic Mechanical Characterization

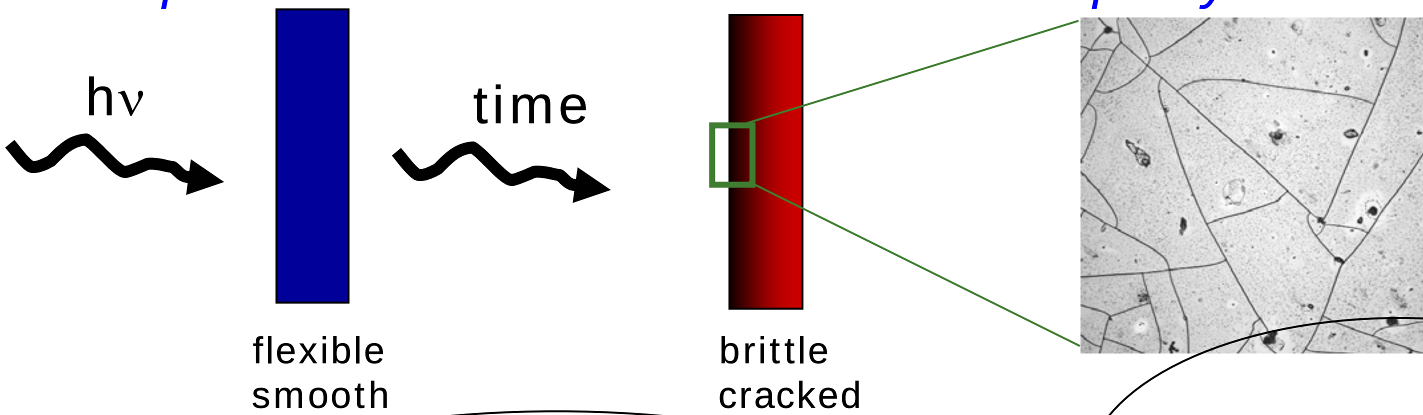
Oscillate tip at sample surface

$$E_r' = \left[\frac{P_0}{\Delta h_0}\cos\delta\right]\frac{\sqrt{\pi}}{2\sqrt{A}} = \frac{S\sqrt{\pi}}{2\sqrt{A}}, \text{ elastic}$$

$$E_r'' = \left[\frac{P_0}{\Delta h_0}\sin\delta\right]\frac{\sqrt{\pi}}{2\sqrt{A}} = \frac{C\omega\sqrt{\pi}}{2\sqrt{A}}, \text{ viscous}$$

Technical Approach

Incorporation of Surface Mechanical Property Measurements



@ the top 1-3 microns of the surface

creep and stress relaxation

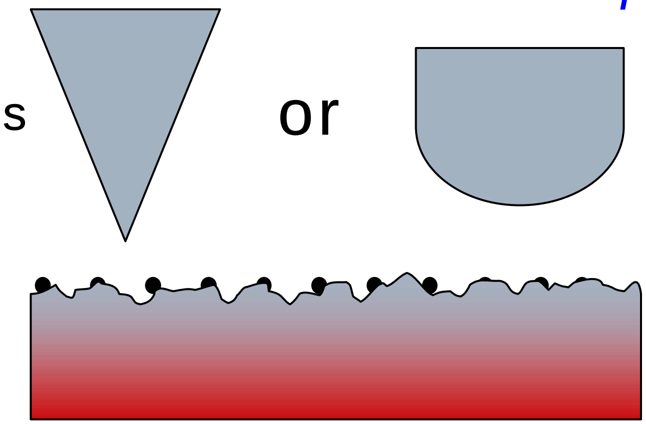
Quantitative Modulus and Hardness

Quantitative Storage and Loss Modulus

a: Viscoelastic Characterization
b: Failure indicators that signal the onset of failure modes (chalking, brittleness, cracking)

Why is this difficult?

Incorporation of Surface Mechanical Property Measurements



- **Contact radii are 2 – 10 micron and depths of 1 – 3 micron**
- **Tip-sample interaction must be characterized**
  - **Roughness**
  - **Presence of particles and particle geometry**
  - **Effects of tip geometry**
- **Multiple approaches for polymer analysis**
  - **No stand-outs**
  - **No clear method for difficult samples**

Relationship between dispersion, chemistry, and mechanical properties for small volumes

Gantt chart - Organization

Y1	Y2	Y3	Y4

Quasi-static measurements

Modulus and Hardness – comparison to bulk
Link to failure indicators
Link to particle, dispersion, surface characteristics

Dynamic Measurements

Creep and Stress Relaxation Dynamic Mechanical (E'and E")

Comparison to bulk

Link to failure indicators and film characteristics

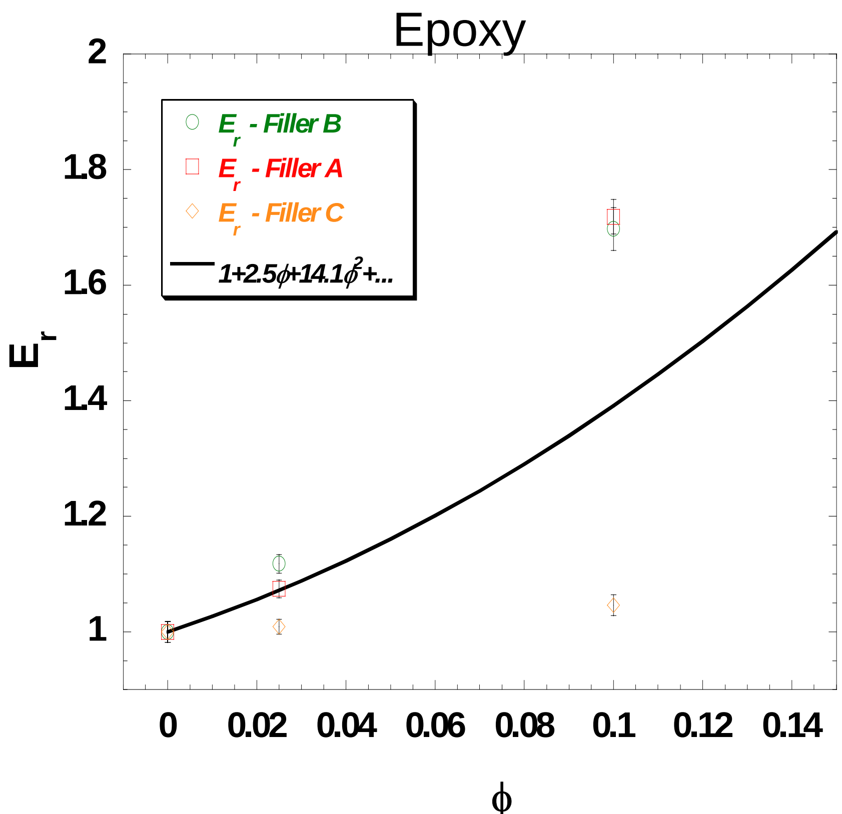
New Techniques*

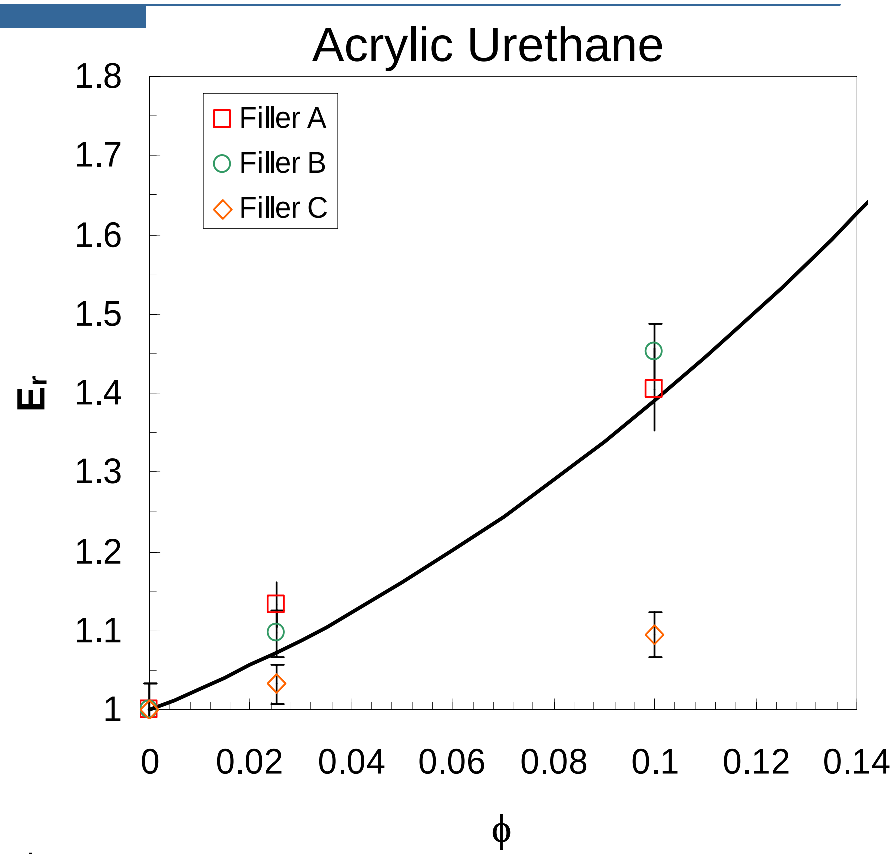
New metrologies for increasing resolution and accuracy

Continually refine and improve current measurement techniques and advance data analysis

***: investigate additional mechanical property measurement methods**

Particle Dispersion Effects Modulus



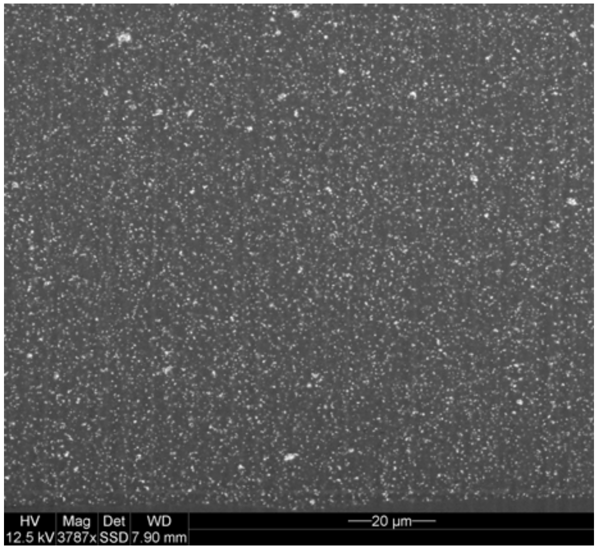


- Quantifying dispersion is important
- Solid line is the theoretical model → $E_r = 1 + 2.5\phi + 14.1\phi^2$
- Particle volume concentration (ϕ) is not accurate with nanoparticles

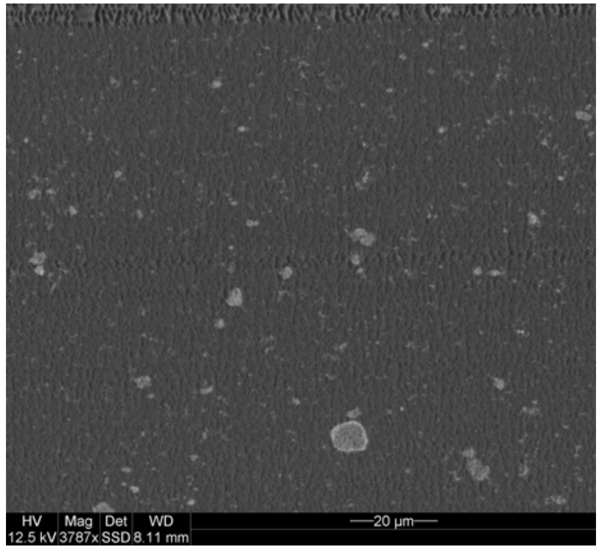
*Error bars represent one standard deviation

Particle Dispersion in Films - SEM

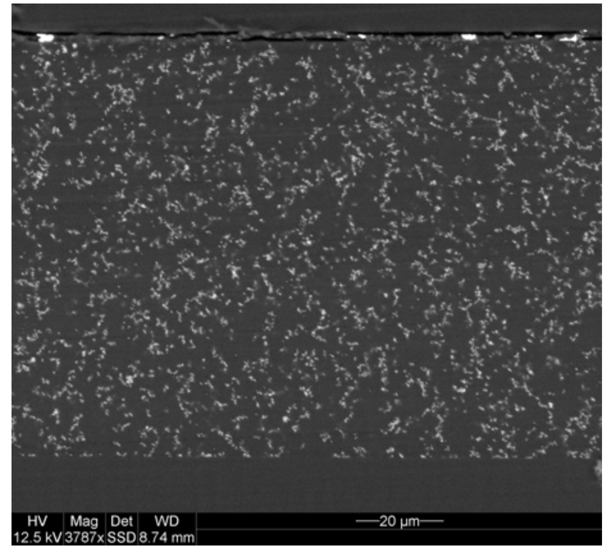
Acrylic Urethane
Filler B (250 nm), 2.5%



Acrylic Urethane
Filler C (20 nm), 2.5%

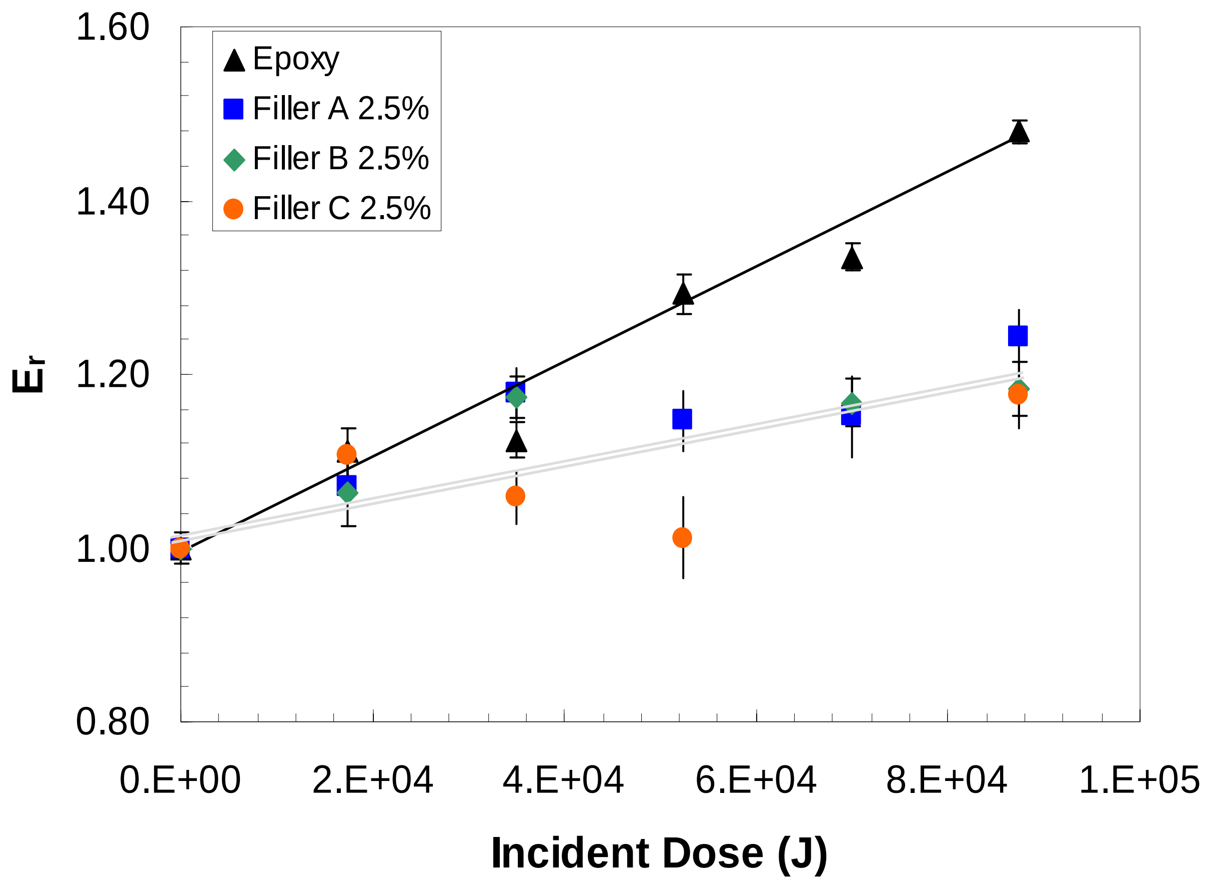


Epoxy
Filler B (250 nm), 2.5%



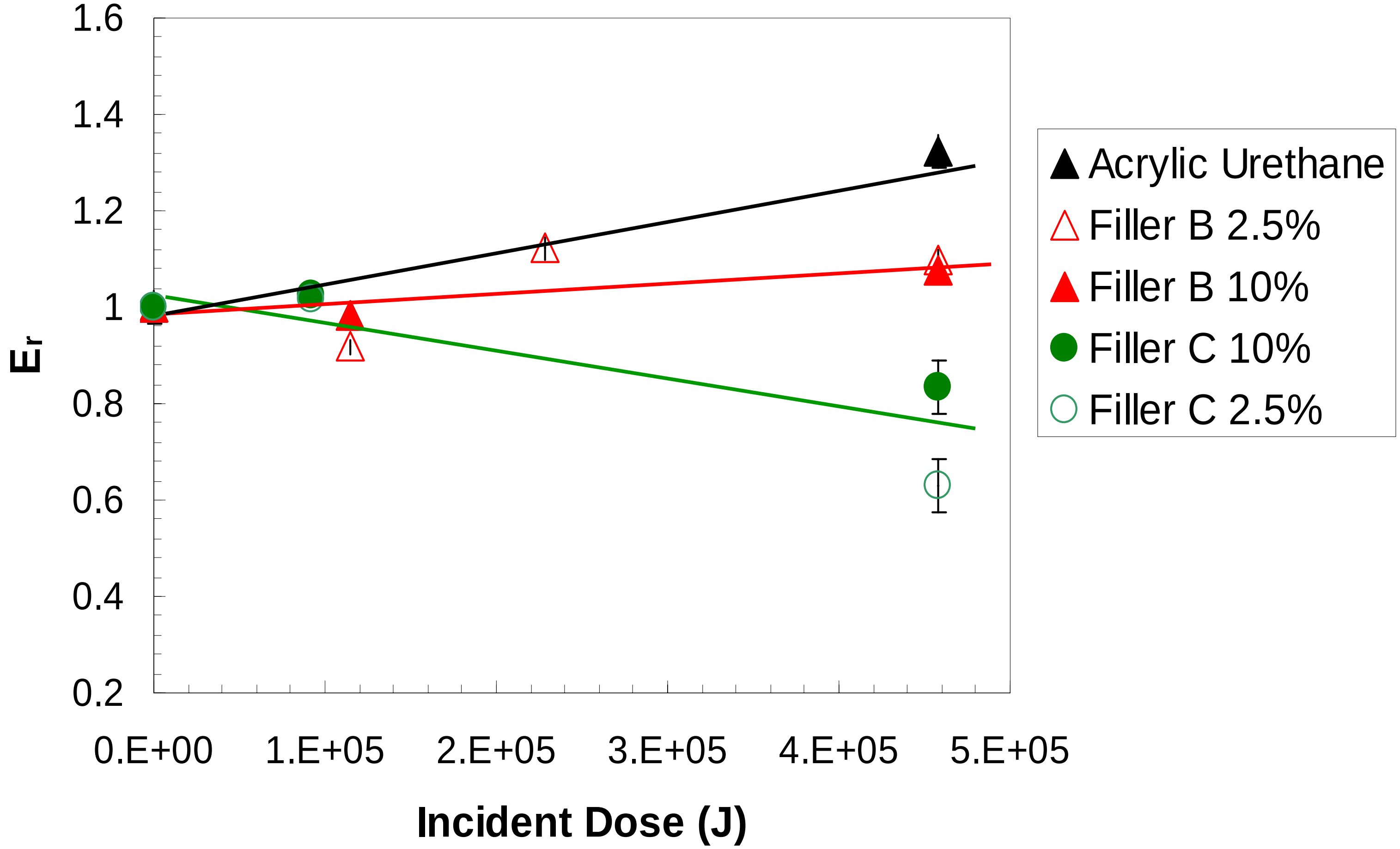
- SEM image of sectioned films (microtomed) before degradation
- The lack of dispersion in AU Filler C and Epoxy Filler B are evident
- AU Filler B has much better dispersion, but clumps are still present

No Difference in Pigment for Filled Epoxies



*Error bars represent 95% confidence levels

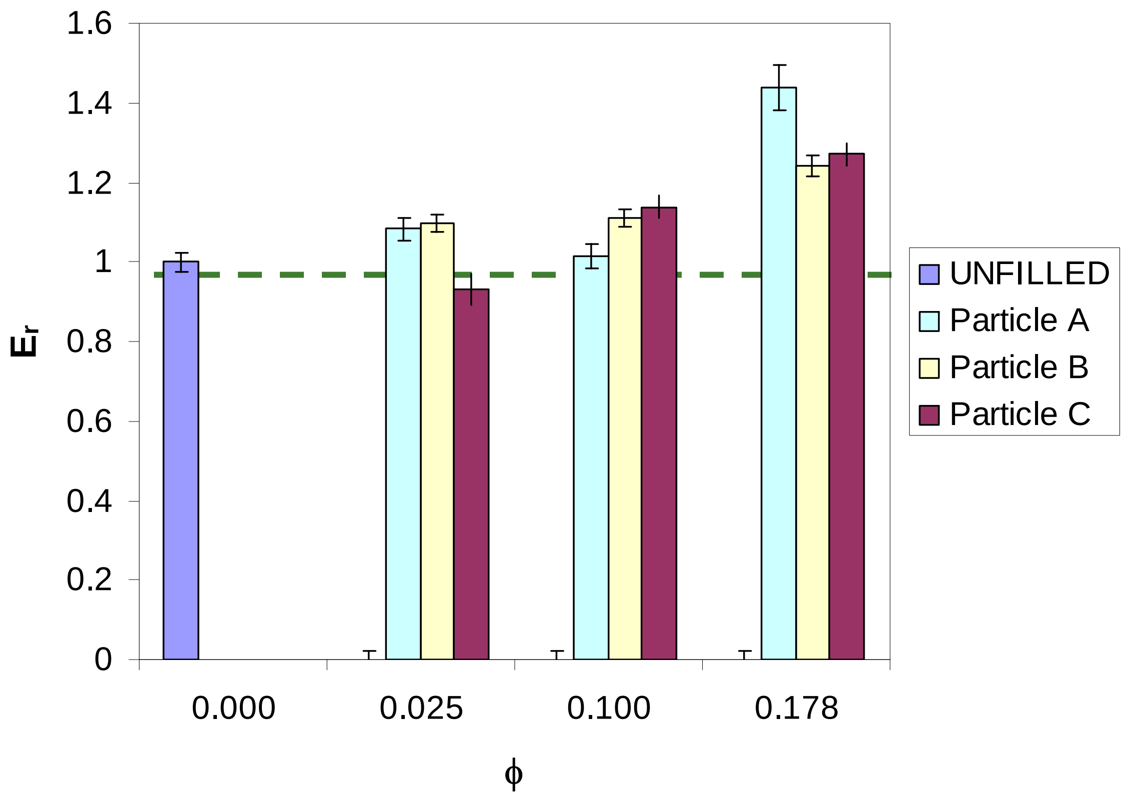
Differences in Pigment for Acrylic Urethane

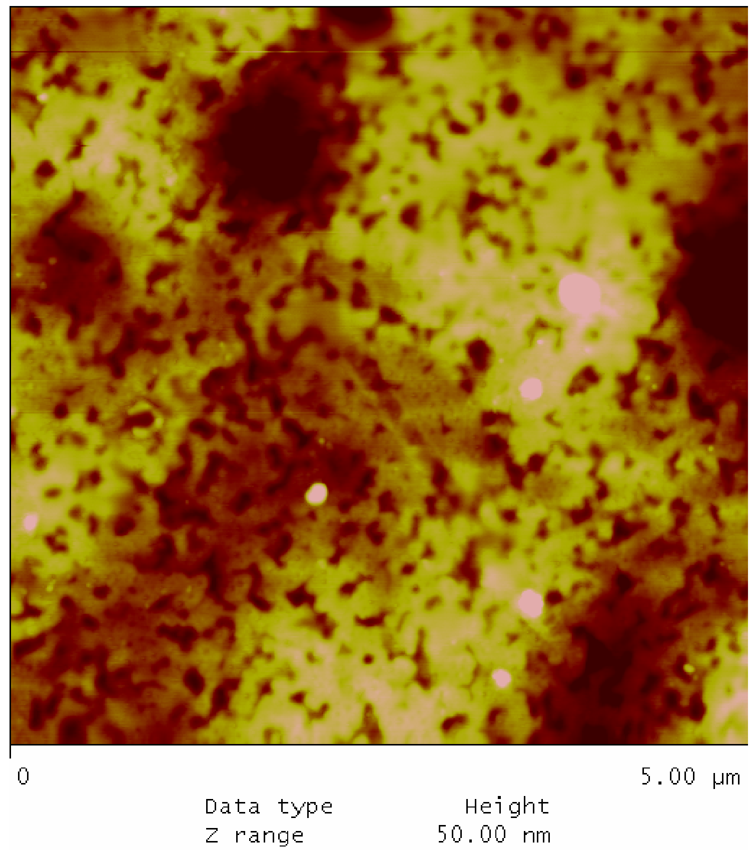


Are the differences dispersion or photoreactivity?

*Error bars represent one standard deviation

Styrene-Acrylic Latex Exhibits Less Stiffening





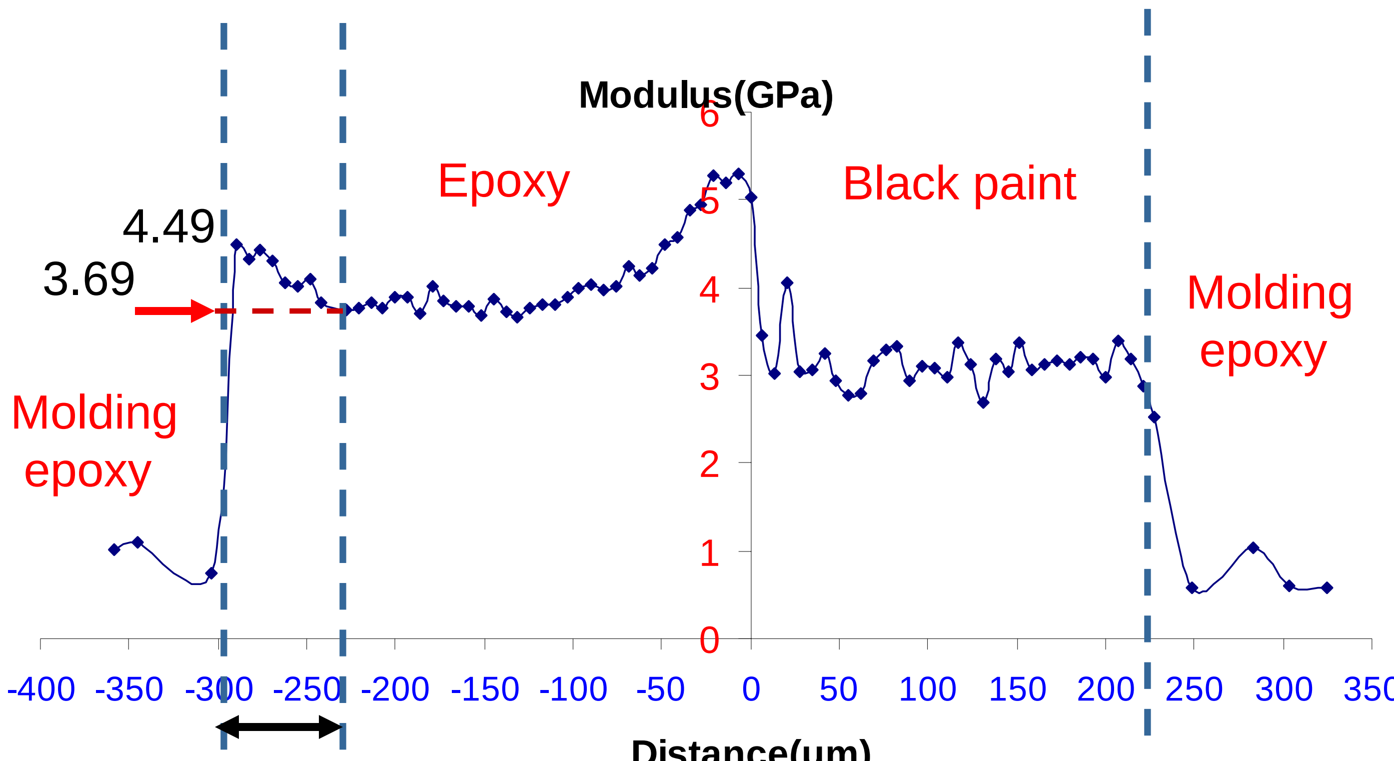
†AFM courtesy of X. Gu

Difference in Film Morphology for Latex

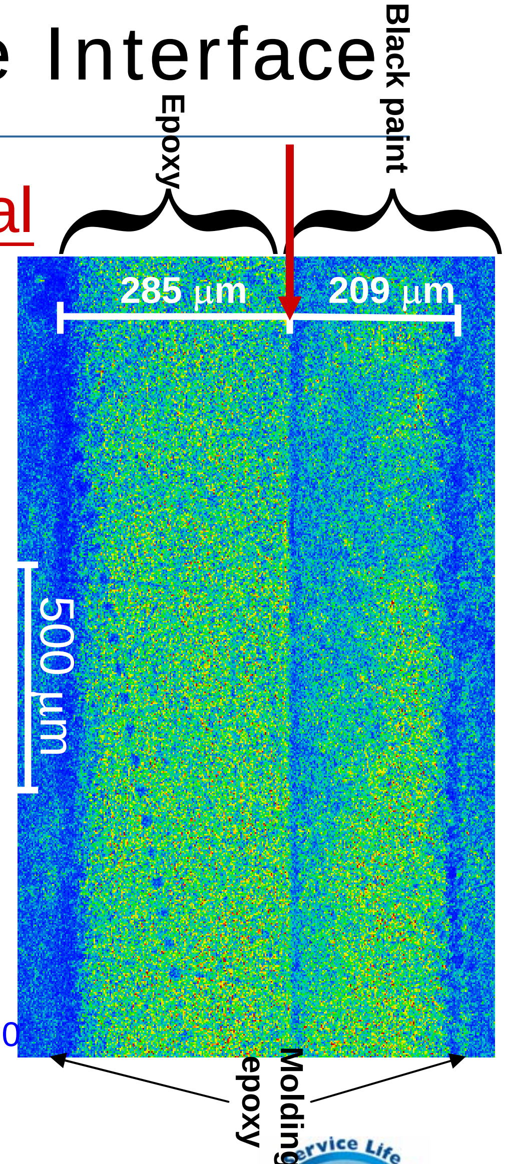
*Error bars represent one standard deviation

Elastic Modulus Quantified Across the Interface

Nanoindentation



Confocal

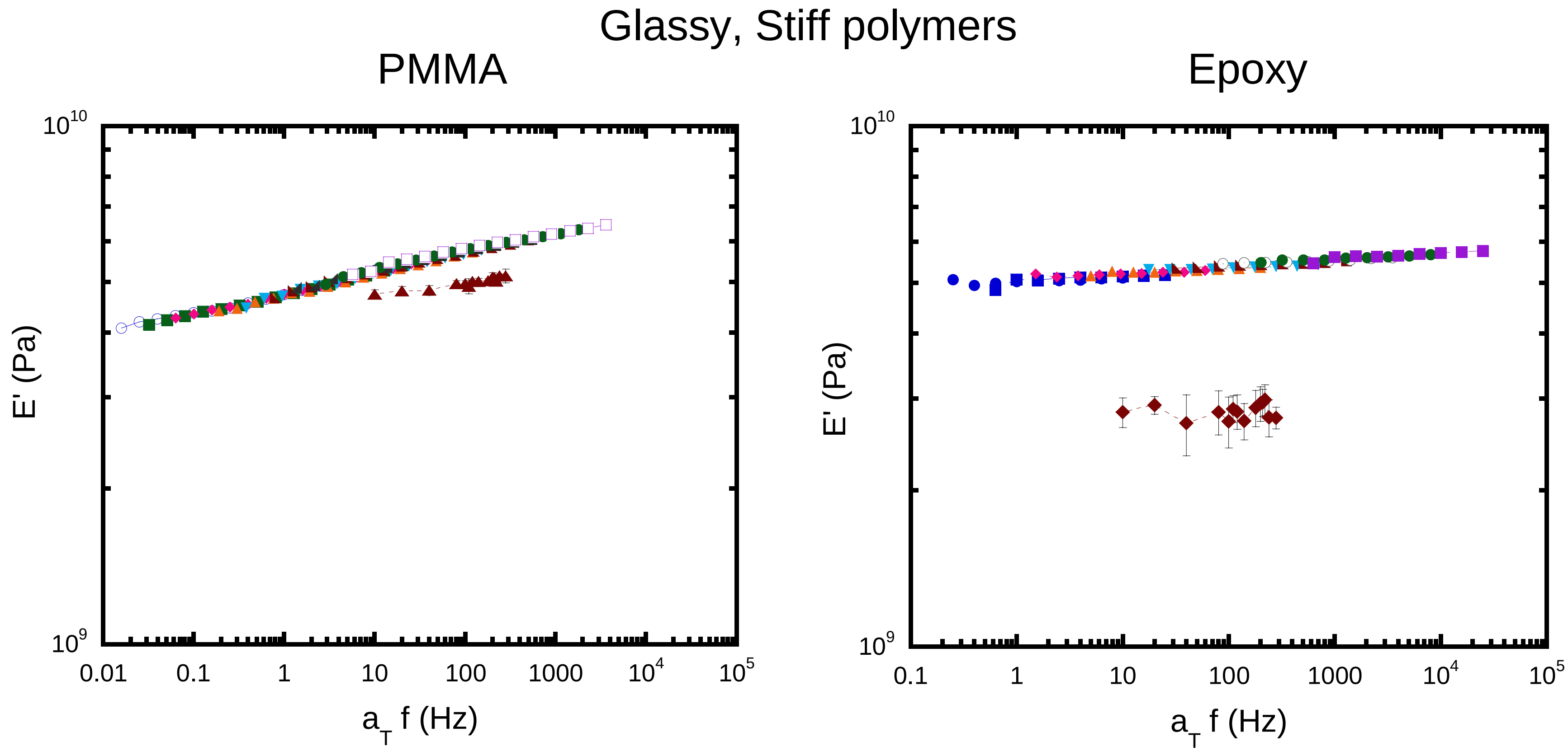


X. Gu, P. Drzal, et al.

Fresh Epoxy: Modulus (3.8 Gpa ± 0.1Gpa)

Degraded Sample: Surface Modulus (5.0 Gpa ± 0.1Gpa)

Dynamic Measurements depend on Film Properties

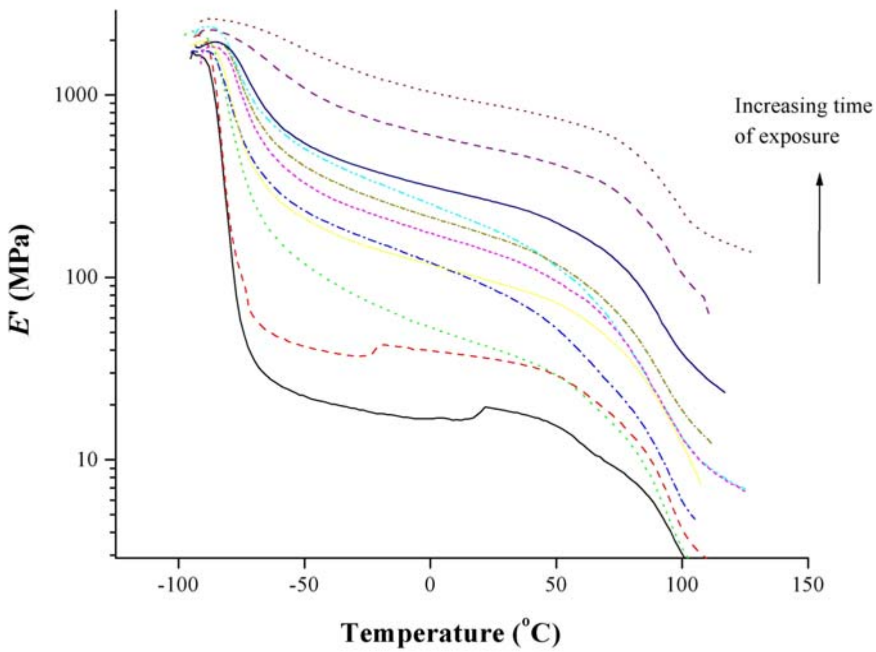


- Tip-sample interactions
- Viscoelastic materials

P. Drzal, M. VanLandingham, et al.

Storage Modulus Increases with Crosslinking

Bulk mechanical measurements of a rubbery sealant material exposed to accelerated weathering conditions



- Dynamic mechanical thermal analysis: Temperature sweep undertaken at 1Hz from -100°C to 120°C.
- Indication for **macroscopic cross-linking** occurs.
- Transition between glassy modulus and rubbery modulus become less distinctive, indicating specimens become more **heterogeneous**.

Exposure environment: 30°C and 0% relative humidity

*C. White, NIST

Summary

- Conduct modulus measurements on filled/unfilled coatings
  - Epoxy, acrylic urethane, and latex
  - Bulk measurements on sealant materials
- Track changes in modulus at the surface of the coatings throughout the degradation cycle
  - Epoxy and acrylic urethane
- Challenges remain:
  - Effect of roughness
  - Influence of particle size, dispersion
  - Viscoelastic characterization of degraded surfaces
  - Tip-Sample interaction

Gantt chart – Progress Metrics

Y1	Y2	Y3	Y4

Quasi-static measurements

- Modulus – comparison to bulk
- failure indicators – identified
- correlations to dispersion, photoreactivity, and chemistry

Viscoelastic Measurements

- Storage and loss modulus – ability to measure and comparison to bulk
- Creep and stress relaxation - ability to measure and comparison to bulk
- Correlations to dispersion, photoreactivity, and chemistry
- Modeling the tip-sample interaction

Impact

- Develop methodologies that relate mechanical properties (quasi-static and dynamic) to durability analysis

- A link between filler chemistry, dispersion, and mechanical properties that is incorporated into service life prediction
  - Scales from constituent to coating performance

- Fundamental material system chosen and evaluated for performance metrics
  - engineered durability – cheaper, better, faster!

Acknowledgements

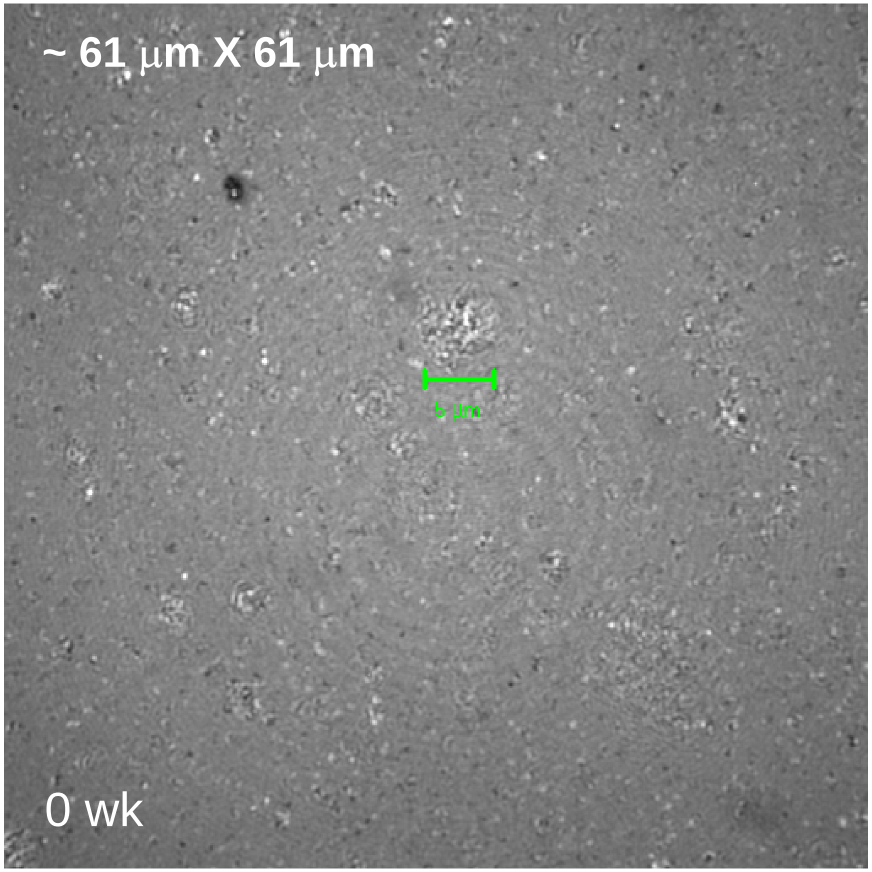
- Pete Drzal – PPG
- Stephanie Watson – NIST
- Amanda Forster - NIST
- LiPiin Sung – NIST
- Xiaohong Gu – NIST
- Jeff Comer – Cal Poly
- Laura Johnson – Cal Poly
- Tom Juliano – Army Research Laboratory

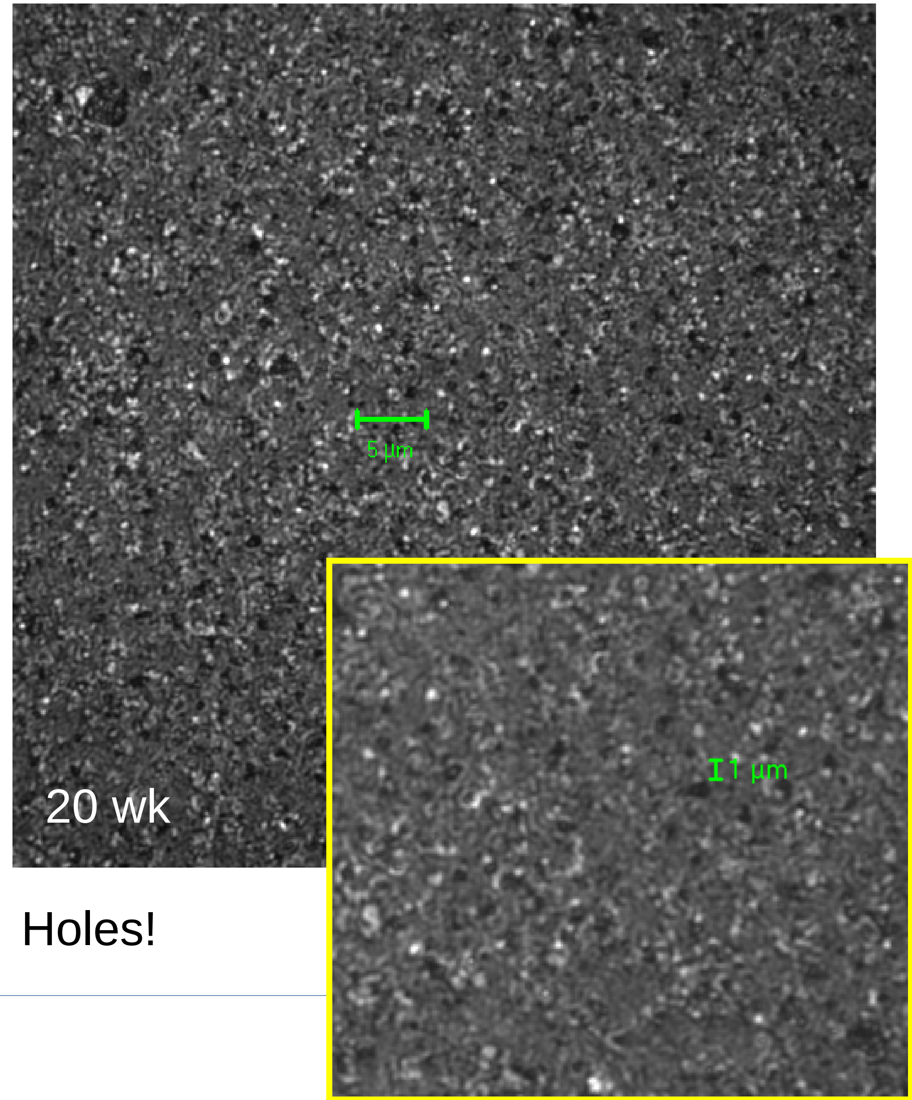
The End

Questions?

Particle Dispersion in Films - Confocal

Acrylic Urethane - 2.5 % Filler C



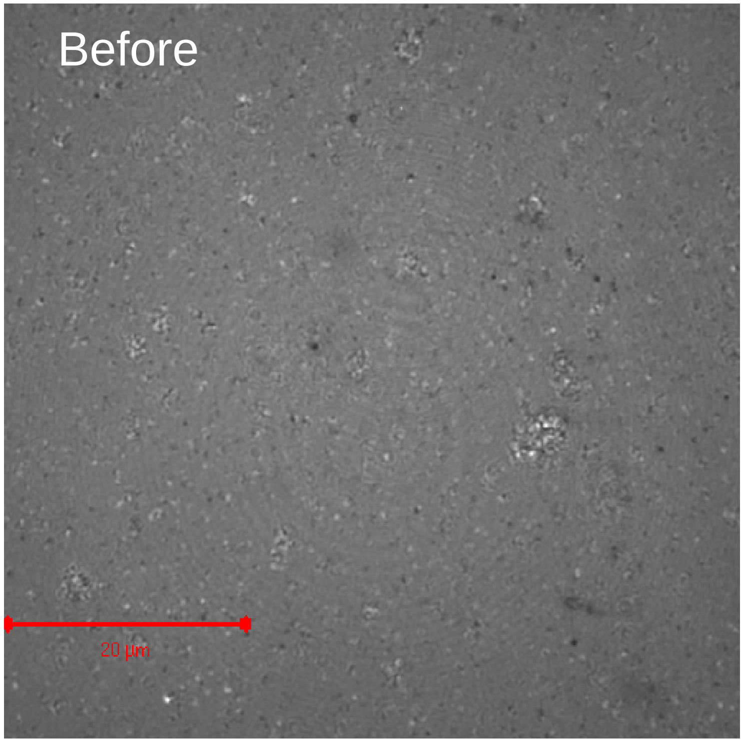


Pigment Clumps: poor dispersion

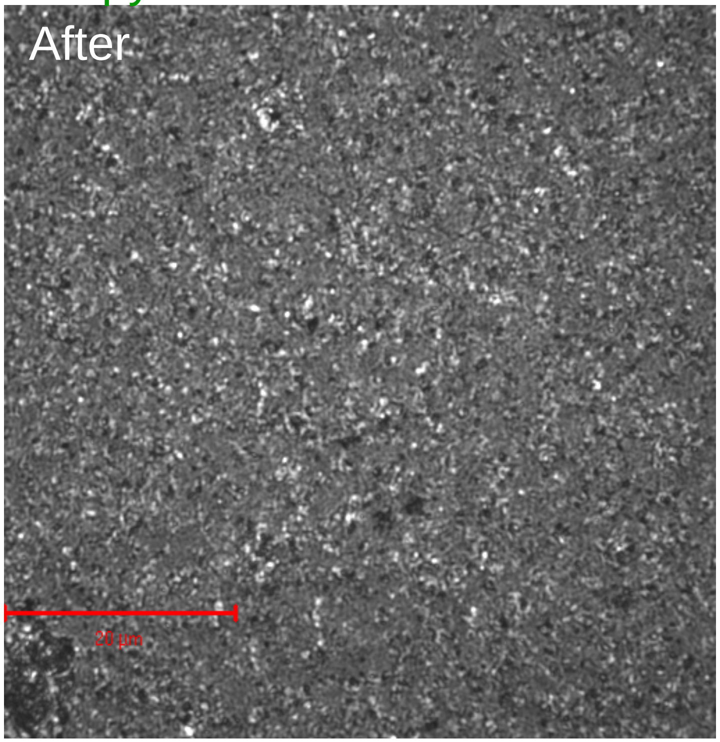
Holes!

Film Topography After Degradation

Confocal Microscopy



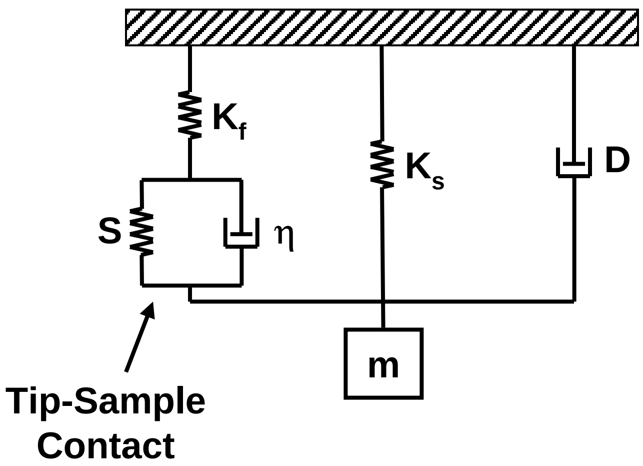
$Sq = 0.067\ \mu m$



$Sq = 0.181\ \mu m$

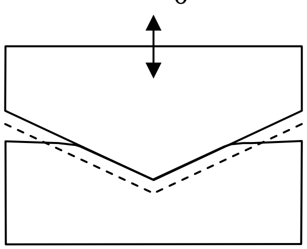
- 2D projection image (150x), scale bar is 20 µm, area is 60 µm x 60 µm
- Increase in surface roughness, exposure of pigment, and pitting occur with increased exposure (20 weeks)
- Presents a challenge for indentation and ATR measurements

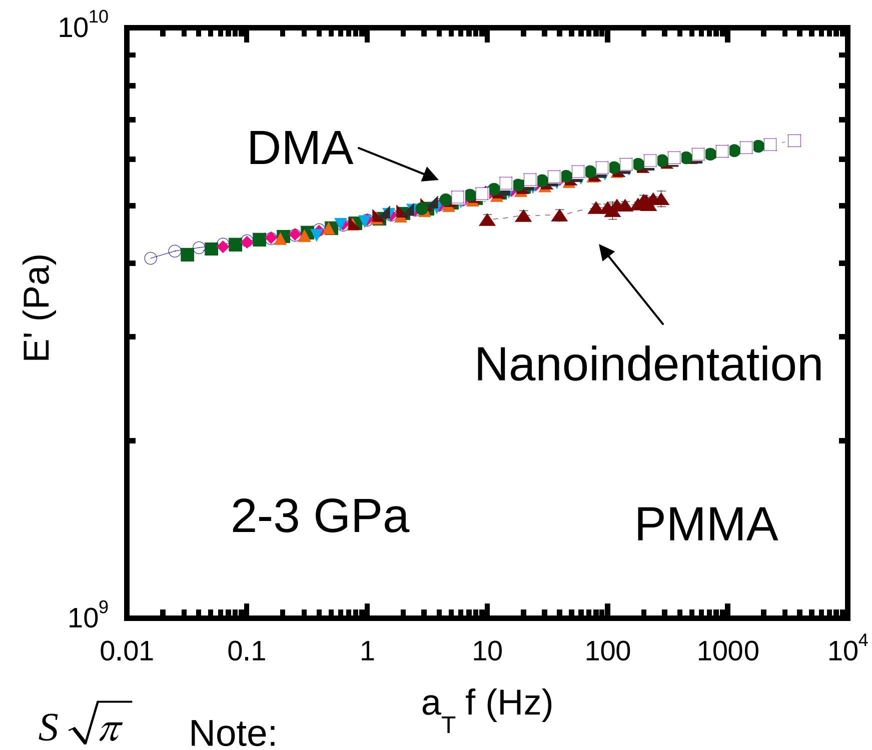
Dynamic Mechanical Characterization



$$\Delta h = \Delta h_0 e^{i(\omega t + \delta)}$$

$$P = P_0 e^{i\omega t}$$





$$E_r' = \left[\frac{P_0}{\Delta h_0}\cos\delta\right]\frac{\sqrt{\pi}}{2\sqrt{A}} = \frac{S\sqrt{\pi}}{2\sqrt{A}}$$

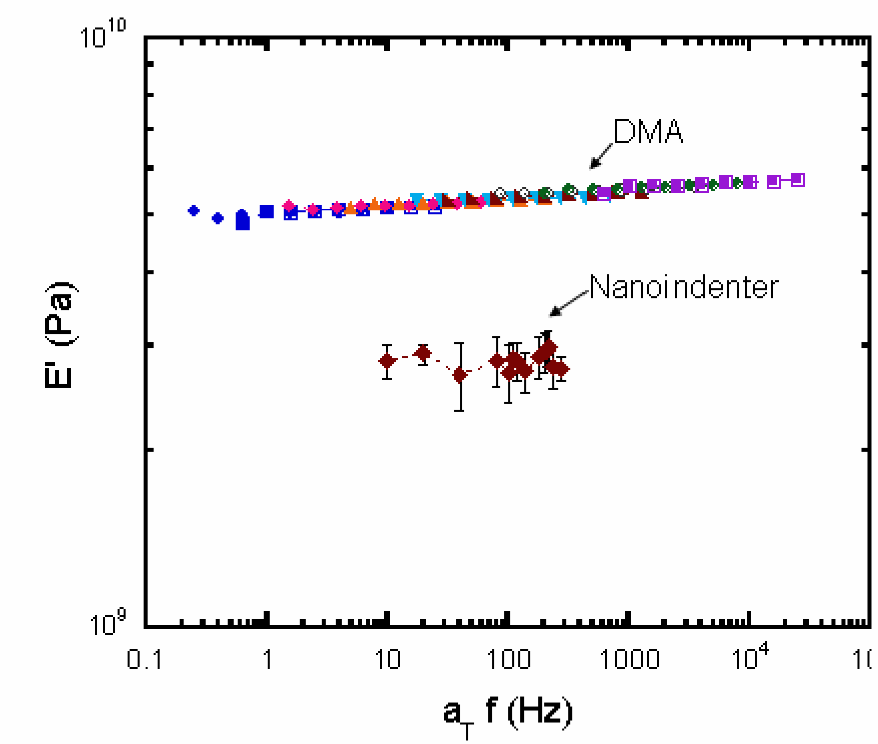
$$E_r'' = \left[\frac{P_0}{\Delta h_0}\sin\delta\right]\frac{\sqrt{\pi}}{2\sqrt{A}} = \frac{C\omega\sqrt{\pi}}{2\sqrt{A}}$$

Note:
- Works well on glassy and elastomeric materials
- Sample volume is changing
- Assumes harmonic unloading is elastic
- Most polymers are viscoelastic!
- Soft materials require large contacts
- Beware of treating like a black box

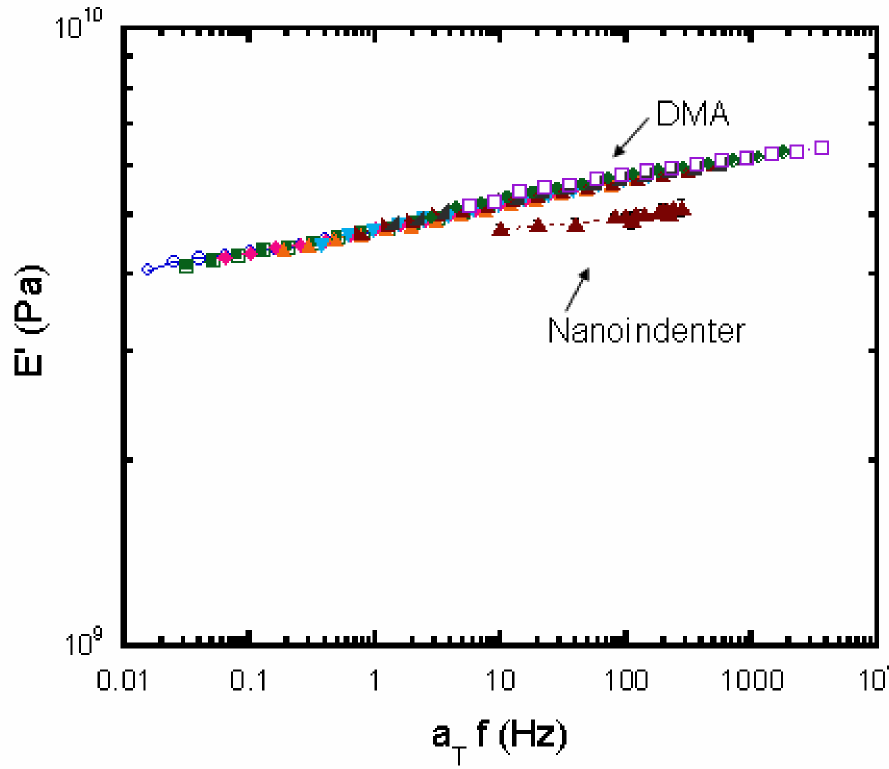
Courtesy of P. Drzal

Dynamic Measurements

Epoxy



PMMA



The agreement is pretty good

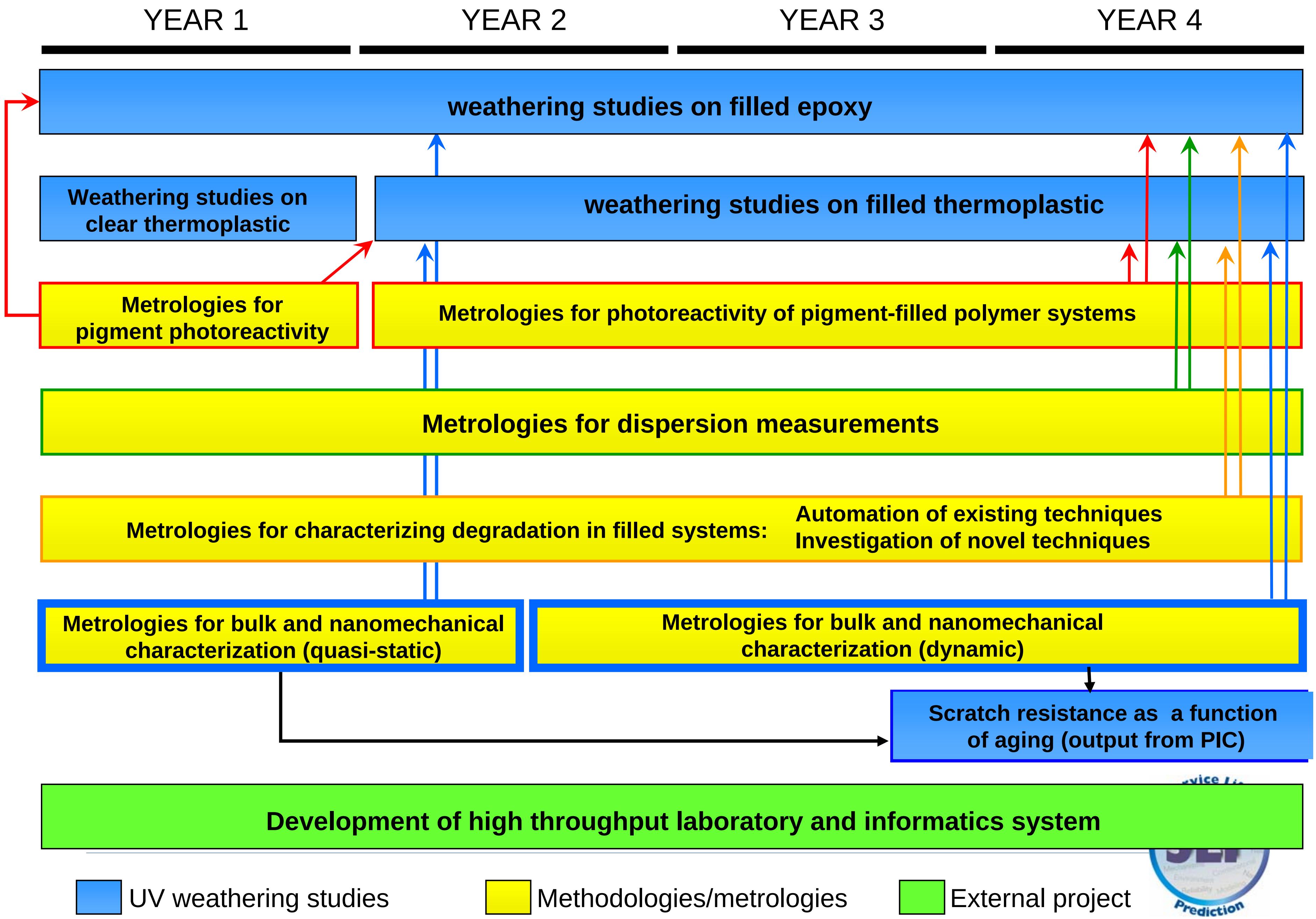
The Epoxy has more strain dependence.

Dynamic Properties

$$E_r' = \frac{S\sqrt{\pi}}{2\sqrt{A}} \qquad E' = \frac{\sqrt{\pi}}{2\sqrt{A}}\left(\frac{P_0}{h_0}\cos\delta\right)$$

$$E_r'' = \frac{\omega C_s\sqrt{\pi}}{2\sqrt{A}} \qquad E'' = \frac{\sqrt{\pi}}{2\sqrt{A}}\left(\frac{P_0}{h_0}\sin\delta\right)$$

This analys is a good starting place, but should fail when the materials show any viscoelastic nature. The geometry of the nanoindentor does not approximate the gap loading conditions.



YEAR 1
YEAR 2
YEAR 3
YEAR 4
weathering studies on filled epoxy
Weathering studies on clear thermoplastic
weathering studies on filled thermoplastic
Metrologies for pigment photoreactivity
Metrologies for photoreactivity of pigment-filled polymer systems
Metrologies for dispersion measurements
Metrologies for characterizing degradation in filled systems:
Automation of existing techniques
Investigation of novel techniques
Metrologies for bulk and nanomechanical characterization (quasi-static)
Metrologies for bulk and nanomechanical characterization (dynamic)
Scratch resistance as a function of aging (output from PIC)
Development of high throughput laboratory and informatics system
UV weathering studies
Methodologies/metrologies
External project
Prediction

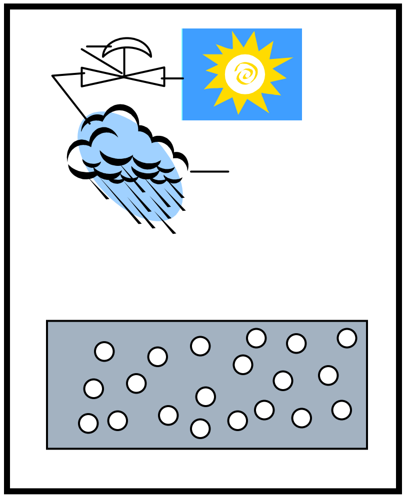
Motivation

- Commercial coatings add particles (pigments) as filler
  - Improves optical properties
    - Whiteness, brightness, opacity, …
  - Improves mechanical properties
    - Scratch resistance, modulus, …

- TiO_2 is a semiconducting material that is commonly used
  - Photoreactivity implications for coating performance
    - Changes in photodegradation mechanisms

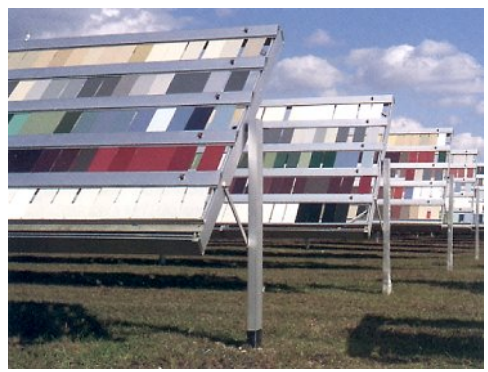
- Questions:
  - *Does photoreactivity affect weatherability?*
  - *How do surface mechanical properties change with weathering?*
  - *Do mechanical changes correlate to thermal or chemical measurements at the degraded film surface?*

New Technical Idea



Indoor

Additivity
Reciprocity



Outdoor

Service Life Prediction
Clear Coatings

- *indoor now drives performance metrics because moved to a dosage model*